Colligative Properties
&
their application

Notes prepared
by

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Quantitative ways of expressing Concentrations

- Concentration is the proportion of a substance in a mixture, so it is an ***intensive*** property. It does not depend on the quantity of the mixture present. e.g. 1 L of 0.1M NaCl has the same concentration as 1.0 ml of 0.1M NaCl.
- Concentration is often expressed as the ratio of quantity of ***solute*** to the quantity of ***solution.*** Sometimes it is the ***ratio*** of ***solute*** to ***solvent.***
- Several concentration terms are employed including:
- Molarity (M)
- Molality (m)
- Ppm (parts per million)
- Ppb (parts per billion)
- Ppmv (parts per million by volume)

$$\text{Molarity} = \frac{\text{Amount of solute (in moles)}}{\text{Volume of solution in L}}$$

$$\text{Molality} = \frac{\text{Amount of solute in moles}}{\text{Mass of solvent in kg}}$$

$$\text{Parts per million} = \frac{\text{mass of solute}}{\text{mass of solution}}$$

$$\text{Parts per volume} = \frac{\text{Volume of solute}}{\text{Volume of solution}}$$

$$\text{Mole fraction} = \frac{\text{amount of solute in moles}}{\text{Total amount of solute in moles} + \text{amount of solvent in mole}}$$

- Molarity (M) = is the number of moles of solute dissolved in 1L of solution.

$$Molarity = \frac{moles\ of\ solute}{volume(L)\ of\ solutio}$$

Because V (volume) is affected by T, it follows that molarity is also affected by T. This error can be eliminated by using *molality (m)* which does not depend on T.

Molality (m) is defined as : the number of moles of solute dissolved in 1kg of solvent.

$$molality = \frac{amount(moles)\ of\ solut}{mass(kg)\ of\ solvent}$$

- What is the molality of solution prepared by dissolving 32.0 gm $CaCl_2$ in 271 gm of water?
- Convert gm to mole

$$moles\ of\ CaCl_2 = 32x\frac{1\ mole\ of\ CaCl_2}{110.98\ gm\ CaCl_2} = 0.288\ moles$$

$$Molality\ of\ CaCl_2 = \frac{moles\ of\ solute}{kg\ of\ solvent} = \frac{0.288}{271x\frac{1kg}{1000g}} = 1.06m\ CaCl_2$$

Parts of solute by parts of solution
a-by mass

$$mass\ percent = \frac{mass\ of\ solute}{mass\ of\ solute + mass\ of\ solvent}\ x100$$

$$mass\ percent = \frac{mass\ of\ solute}{mass\ of\ solution}\ x100$$

$$sometimes\ mass\ percent\ is\ presented\ as\ \%w/w$$

Parts of solute by parts of solution
b-by volume

- Most widely used is parts by volume percent, the volume of solute in 100 volumes of solution.

$$Volume\ percent = \frac{volume\ of\ solute}{volume\ of\ solution} x 100$$

- A common symbol for volume percent is % (v/v)

ppm & ppb

- Ppm = parts per million= gm of solute per million parts of solution
- Ppb = parts per billion=gm of solute per billion parts of solution

$$ppm = \frac{mass\ of\ solute}{mass\ of\ solution} x10^6$$

$$ppb = \frac{mass\ of\ solute}{mass\ of\ solution} x10^9$$

Ppmv= parts per million by volume

- Examples: Find the concentration of Ca in ppm in 3.5 g pill that contain 40.5 mg of Ca.

$$ppm\,of\,Ca = \frac{mass\,of\,calcium}{mass\,of\,pill}\,x\,10^{6} = \frac{40.5\,mg\,x\,\frac{1\,gm}{10^{3}\,mg}}{3.50}\,x\,10^{6} = 1.16\,x\,10^{4}\;ppm\,of\,Ca$$

- A sample of rubbing alcohol contains 142 g of isopropyl alcohol C_3H_7OH and 58.08 of water. What are the mole fraction of alcohol and water.

$$\text{Convert from gms to moles:}$$

$$\text{moles of } C_3H_7OH = 142\,g\ C_3H_7OH \text{ x } \frac{1 \text{ mole } C_3H_7OH}{60.9\ C_3H_7OH} = 2.36 \text{ mole } C_3H_7OH$$

$$\text{moles of } H_2O = 58\,g\ H_2O \text{ x } \frac{1 \text{ mole of } H_2O}{58.02\,g\ H_2O} = 3.22 \text{ moles of } H_2O$$

$$\text{Calculation of mole fraction for water} = \frac{\text{mole of } H_2O}{\text{total moles}} = \frac{3.22}{2.36 + 3.22} = 0.423$$

$$\text{mole fraction for alcohol} = \frac{2.36}{2.36 + 3.22} = 0.577$$

$$\text{Remember that the sum of mole fractions} = 1, \text{ therefore we can write } 1 - 4.23 = 0.577$$

What do we mean by colligative properties?

- In simple terms it means “COLLECTIVE”
- We might expect the presence of ***solute*** particles to make the physical properties of solution different from those of the pure solvent. However we might ***no***t expect is that , in the case of four important solution properties. the ***number of solute particles*** makes the difference, ***not their chemical identity***.
- These properties are known as colligative properties which are :
  - Vapor pressure lowering
  - Boiling point elevation
  - Freezing point depression
  - Osmotic pressure

Even though most of these effects are small, they have many practical applications as will be seen later.

- Colligative properties were measured first to explore the dissociation of solute in the solvent. From our past knowledge, electrolytes can be either strong, or weak which conduct electricity to varying degrees. On the other hand non-electrolytes do not conduct electric current simply because they do not form “ions” in solution.
- To predict the magnitude of a colligative property, we refer to the ***solute formula*** to find the number of particles in the solution .e.g. each mole of solute yield one mole of particles in the solution. e.g 0.35M of glucose yield 0.35 Mol of solute per liter.
- In principle, strong electrolytes dissociate into the number of moles of ions in the formula unit. e.g. 0.4 Mol of Na_2SO_4 contains 0.8 mole of Na^+ and 0.4 mole of SO_4^{2-} ions. The total would be 1.2 M particles in 1L of solution

Colligative properties of ***non-volatile non-electrolyte solutions***

- **Vapour pressure lowering:**ΔP
- The vapour pressure of a solution of non-volatile non-electrolyte is always lower than the vapour pressure of the pure solvent.

  Raoult's law: state that the vapour pressure of solvent in the vapour phase above the solution $= P_{solvent}$

  $P_{solvent} = X_{solvent} \times P^{o}{}_{solvent}$

  in solution, $X_{solvent}$ is always less than 1.This implies that

  $P_{solvent}$ is less than $P^{o}{}_{solvent}$

An ideal solution is one which obey's Raoult's law at all concentrations. In practice this only applies to dilute solutions; the more dilute , the more they obey the law.

How does the amount of solute affect the magnitude of the vapour pressure lowering ΔP

- The solution consists of solvent and solute so the sum of their mole fractions = 1.

$X_{solvent} + X_{solute} = 1$ *thus* $X_{solvent} = 1 - X_{solute}$

From Raoult's law :

$P_{solvent} = X_{solvent} \times P^{o}_{solvent} = (1 - X_{solute}) \times P^{o}_{solvent}$

Simplifying we get:

$P_{solvent} = P^{o}_{solvent} - (X_{solute} \times P^{o}_{solvent})$

Therefore:

$$\boldsymbol{P^{o}_{solvent} - P_{solvent} = \Delta P = X_{solute} \times P^{o}_{solvent}}$$

This means that the vapour pressure lowering $\boldsymbol{P^{o}_{solvent} - P_{solvent} = \Delta P}$ for a given solvent ***depends only*** on the ***mole fraction of the solute i.e*** $\boldsymbol{X_{solute}}$ **.**

Boiling point elevation

- **Fact**: A solution boils at a higher temperature than the pure solvent.

  ΔT_b proportinal to molality or $\Delta T_b = K_b m$ where (m) is solution molality , and K_b is prop constant known as the molal boiling point elevation constant
- $\Delta T_b = T_{b(solution)} - T_{b(solvent)}$
- *Note that molality is used and not molarity as the former does not depend on temperature.*
- The units of K_b are $^oC/m$ and is specific for each solvent as illustrated in the following slide;

Solvent	BP °C	K_b (°C/m)	MP °C	K_f (°C/m)
Acetic acid	117.9	3.07	16.60	3.90
Benzene	80.1	2.53	5.50	4.90
Carbon tetrachloride	76.5	5.03	-23.00	30
Diethyl ether	34.5	2.02	-116.20	1.79
Ethanol	78.5	1.22	-117.30	1.99
Water	100.0	0.512	0.00	1.86

Notice: for water K_b is only 0.512 °C/m . If you dissolve 1.00 mole of glucose (180g 1.00 mole of particles) in 1 kg of water, or 0.5 mol of NaCl (29.2g of strong electrolyte so also 1 mol of particles in 1 kg of water, the BP of the resulting solution at 1 atm would be only 100.512.

Freezing point depression ΔT_f

Remember that only solvent molecules can evaporate from the solution, so molecules of the nonvolatile solute are left behind. Likewise, only solvent molecules can solidify leaving solute molecules behind to form a slightly more concentrated solution.

The freezing point of a solution is that temperature at which its vapour pressure equals that of the pure solvent. At this T , the two phases (solid solvent and liquid solution) are in equilibrium.

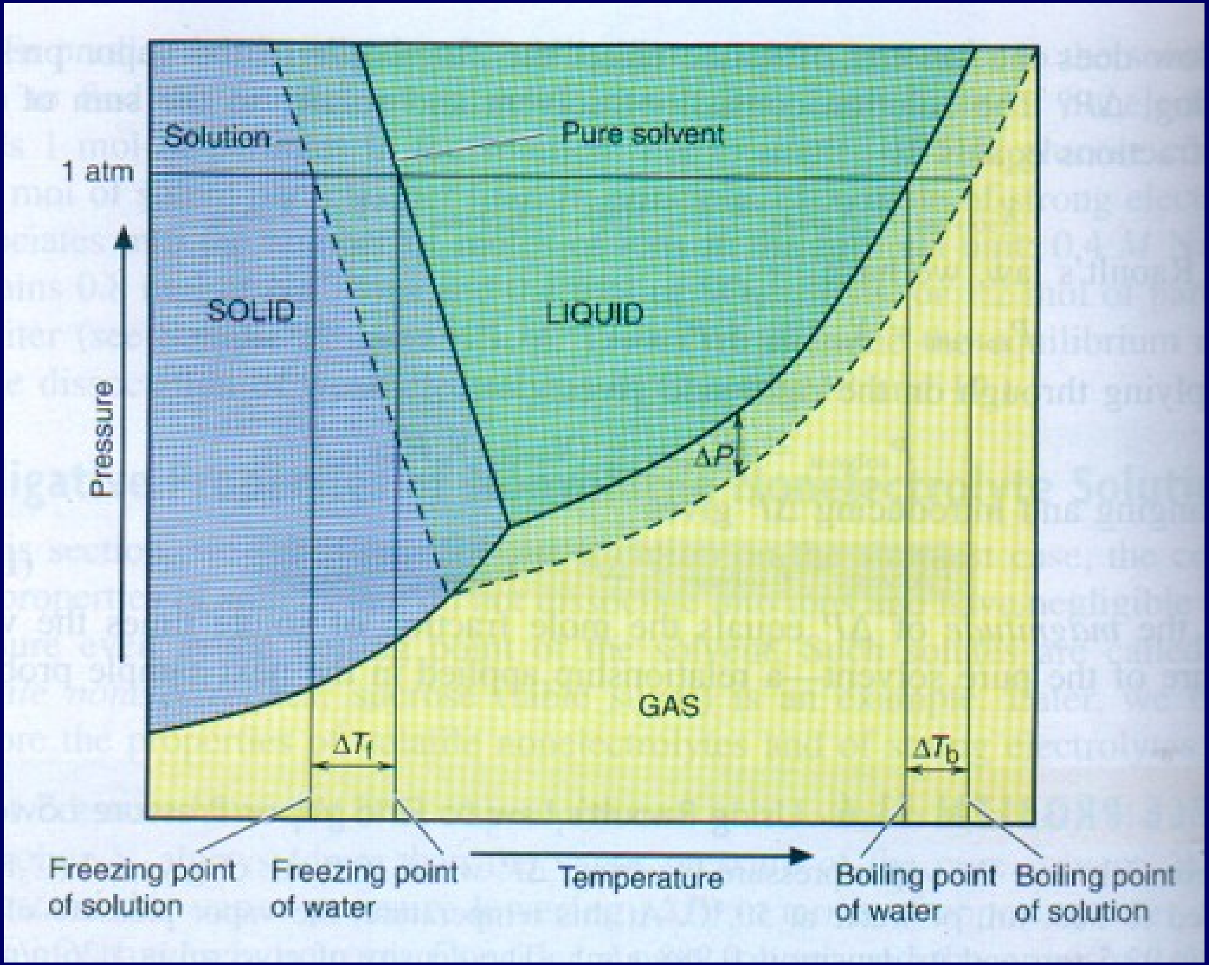
Because the vapour pressure of the solution is lower than that of the solution freezes at lower temperature than the solvent.

In other words, the number of solvent particles leaving and entering the solid per unit time become equal at lower T. *see next slide for the diagram.*

Notice the position of dotted lines

We are interested in the differences only.

The difference must always be a positive in value.



- Like Δ_b the freezing point depression Δ_f has a magnitude proportional to the molal concentration of solute:

$$\Delta_f \; proportional\ to (m)\ i.e. \Delta_f = \mathrm{K}_f\, m$$

- Where K_f is the molal freezing point depression constant. It has units of °C/m . Both K_f and K_b are specific for each solvent as previously noted in the table.
- Example: You add 1 kg of ethylene glycol ($C_2H_6O_2$) antifreeze to your car radiator, which contains 4450 gm of water. What are the boiling and freezing points of the solution?

- First calculate molality by converting the given mass of solute (1.00 kg) to m and divide by mass of solvent which is 4450g.

$$moles\ of\ C_2H_6O_2 = 1.00\,kg\,C_2H_6O_2\ x\ \frac{10^3\,g}{1\,kg}\ x\ \frac{1\,mole\,C_2H_6O_2}{62.07\,g\,C_2H_6O_2} = 16.1\,mol\,C_2H_6O_2$$

$$molality = \frac{mole\ of\ solute}{kg\ solvent} = \frac{16.1\,mol\,C_2H_6O_2}{4450\,g\,H_2O\ x\ \frac{1\,kg}{10^3\,g}} = 3.62\,m\,C_2H_6O_2$$

$$To\ find\ the\ boiling\ point\ elevation,\ we\ look\ up\ in\ the\ table\ the\ value\ of\ \mathrm{K}_b = 0.512\,^oC/m$$

$$Therefore\ \Delta_b = \frac{0.512\,^oC}{m}\ x\ 3.62\,m = 1.85\,^oC$$

$$Therefore\ the\ boiling\ point\ of\ the\ solution = T_{b\,solvent} + \Delta T_b = 100 + 1.85 = 101.85\,^oC$$

In a similar manner we can find first from table, then ΔT_f

$$T_{solution} = T_{solvent} - \Delta_f = 0.00^oC - 6.73^oC = -6.73^oC$$

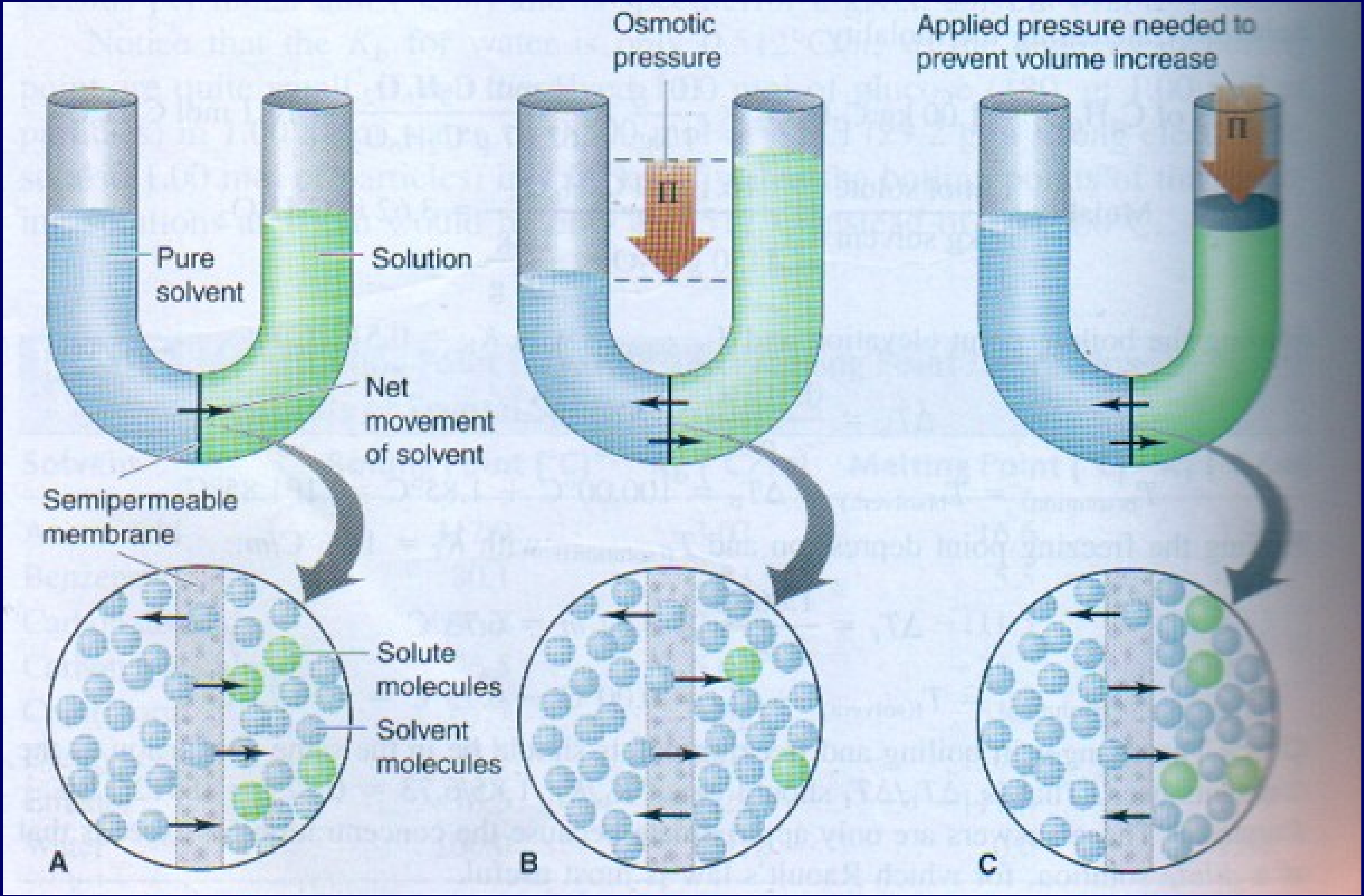
ΔT_f

Please note that the values of and ΔT_b *are positive quantities.*

Explore this statement please.

Osmotic Pressure

- When two solutions are separated by semipermeable membrane (one which allows *solvent* to pass through but not the *solute.)* the solvent moves as in the following diagram:


Osmotic pressure
Applied pressure needed to prevent volume increase
Π
Π
Pure solvent
Solution
Net movement of solvent
Semipermeable membrane
Solute molecules
Solvent molecules
A
B
C

- The height of the solution rises and that of the solvent falls, the resulting pressure difference pushes some water molecules from the solution back through the membrane. At equilibrium, water moves at the same rate in both directions. The pressure difference at equilibrium is the OSMOTIC PRESSURE and usually given the symbol (Π) pi.
- Π is proportional to the number of solute PARTICLES in a given volume of solution , that is to the molarity (*M*)

$$\Pi \ \ prop to \frac{n_{solute}}{V_{solution}} \ \ or \, \Pi \ \ prop to \, M$$

$$The \, prop \, constant \, is \, R \, gas \, constant \, times \, absolute \, temperat$$

$$\Pi = \frac{n_{solute}}{V_{solution}} RT = MRT$$

- Perhaps one of the most important application of this method is to find the molecular weights of substances which are difficult to get in the normal way such as the average molecular weight of polymers.

Application of colligative properties in fractional distillation (volatile nonelectrollyte solutions)

- You may ask what is the effect on vapor pressure when the **solute** is ***VOLATILE,*** that is when the vapor consists of solute & solvent molecules? . From Raoult’s law , we know that:

$$P_{solvent} = X_{solvent} \text{ x } P^{o}_{solvent} \quad \text{Raoult's Law}$$

$$P_{solute} = X_{solute} \text{ x } P^{o}_{solute}$$

where X represents the mole fraction in the LIQUID PHASE

According to Dalton's law of partial pressures, the total vapor pressure is the sum of partial pressures

$$P_{total} = P_{solvent} + P_{solute} = \left(X_{solvent} \text{ x } P^{o}_{solvent}\right) + \left(X_{solute} \text{ x } P^{o}_{solute}\right)$$

$X = 0.5$ for benzene & toluene

vapor pressure of pure benzene at $25\,^{o}C = 95.1\ torr$

and that of pure toluene is 28.4 torr

we need to calculate the partial pressure for each in the liquid phas

$$P_{ben} = X_{ben}\ x\ P^{o}_{ben} = 0.500\ x\ 95.1\ torr = 47.6\ torr$$

$$P_{tol} = X_{tol}\ x\ P^{o}_{tol} = 0.500\ x\ 28.4\ torr = 14.2\ torr$$

- Does the composition of the vapor differ from that of the solution?
- let’s calculate the mole fraction of each substance in the vapor by applying Dalton’s law.

$$X_A = \frac{P_A}{p_{total}}$$

uene in the vapor,

$$X_A = \frac{P_A}{p_{total}}$$

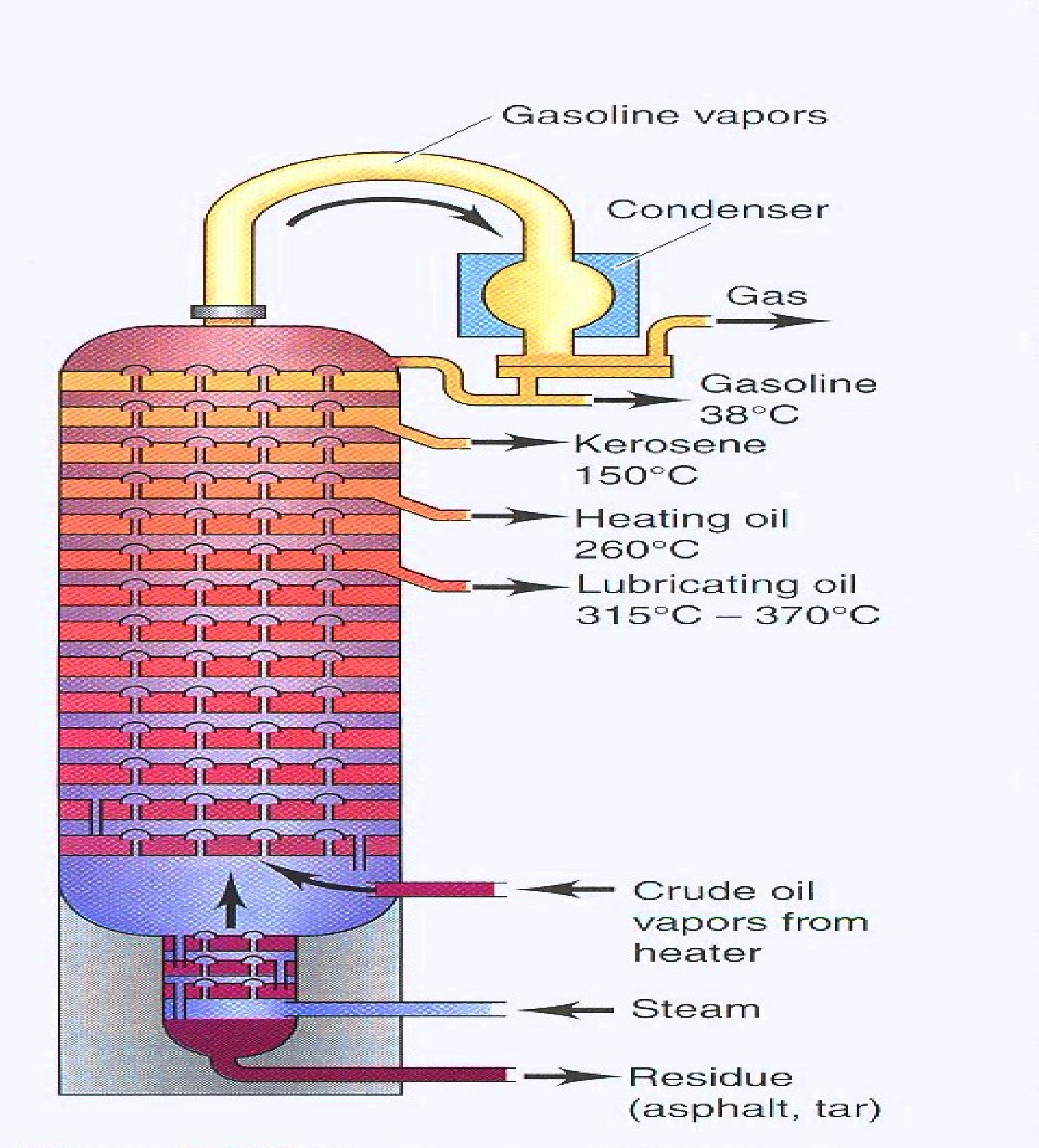
$$X_{benz} = \frac{P_{ben}}{P_{total}} = \frac{47.6}{47.6+14.2} = 0.77 \, tor$$

$$X_{benz} = \frac{P_{tol}}{P_{total}} = \frac{14.2}{47.6+14.2} = 0.23 \, tor$$

Notice that the composition of the vapor phase is different from that of the liquid.

50:50 changed to 77:23

What would happen if the vapor is condensed and reboiled several times?


Gasoline vapors
Condenser
Gas
Gasoline
38°C
Kerosene
150°C
Heating oil
260°C
Lubricating oil
315°C – 370°C
Crude oil
vapors from
heater
Steam
Residue
(asphalt, tar)

Distillation

- Process of vaporizing a liquid, condensing the vapor, and collecting the condensate in another container.
- Uses of Distillation
  - Separating liquids with different boiling points
  - Purifying a liquid.
- Distillation Methods
  1. Simple
  2. Vacuum (at reduced pressure)
  3. Fractional
  4. Steam

Distillation (Con’t)

- **Pure Substance**
  - Temperature remains constant during distillation process so long as both vapor and liquid are present
- **Miscible Liquid Mixture**
  - Temperature increases throughout process because composition of vapor changes continuously.
  - Composition of vapor in equilibrium with the heated liquid is different from the composition of the liquid.

Simple Distillation

- **Single Vaporization / Condensation cycle of a mixture that produces a distillate that is always impure at any temperature range between the range of boiling points of the components.**
- **Therefore, it is impossible to completely separate the components in a mixture with Simple Distillation.**
- **Relatively pure substances can be obtained from a mixture with Simple Distillation if the boiling points of the components differ by a large amount (>100oC)**
- **If a small increment of the initial distillate is separated and redistilled – this process repeated many times, effectively producing multiple sequential Vaporization/Condensation Cycles – an increasingly pure solution can be attained. Processing the entire sample this way would be a very tedious process involving a large number of distillations.**

Fractional Distillation

- Accomplishes the same thing as Multiple Simple Sequential Vaporization / Condensation Cycles, by inserting a Fractionating Column between the Distillation Flask and the Distillation Head.
- The Fractionating Column, of which there are many types containing a variety of packing materials, subjects the mixture to many Vaporization/Condensation Cycles as the material moves up the column toward the Distillation Head, which is attached to the Condenser.
- With each cycle within the column, the composition of the vapor is progressively enriched in the lower boiling liquid.
- This process continues until most of the lower boiling compound is removed from the original mixture and condensed in the receiving flask.

Fractional Distillation (Con’t)

- When the lower boiling liquid is effectively removed from the original mixture, the temperature rises and a second fraction containing some of both compounds is produced.
- As the temperature approaches the boiling point of the higher boiling point compound, the distillate condensing into the third receiving flask is increasingly pure in the higher boiling point compound.

- **Column Efficiency - How pure can you get!!**
  - **A common measure of the efficiency of a Fractionation Column is given by its number of Theoretical Plates.**
  - **One theoretical plate is equivalent to a Simple Distillation, i.e., one Vaporization / Condensation Cycle.**
  - **The smaller the boiling point difference, the greater the number of theoretical plates a fractionating column must have to achieve separation of mixtures**

Boiling point difference	Number of theoretical plates
108	1
54	3
20	10
7	30
4	50
2	100

- Just as a nonvolatile solute lowers the vapor pressure of the solvent by making the mole fraction of the solvent less than 1, the presence of each volatile component lowers the vapor pressure of the other by making each mole fraction less than 1.
- Let’s examine this effect in a solution that contains equal amounts (mol) of henzene (C_6H_6) and toluene (C_7H_5): The number of moles of benzene and toluene are the same = 0.500.
- At 25°C, the vapor pressure of pure benzene (P,) is 95.1 ton and that of pure toluene (Pa,1) is
- 28.4 torr; note that benzene is more volatile than toluene. We find the partial pressures from Raoult’s law: